THE CRYSTAL STRUCTURE OF DIBENZOTHIOPHENE SULFONE

by

Louis R. Kronfeld and Ronald L. Sass
Department of Chemistry, William Marsh Rice University
Houston, Texas

As a part of a study of cyclic sulfones in this laboratory, we have determined the crystal and molecular structure of dibenzothiophene 5,5-dioxide (dibenzothiophene sulfone). The primary interest was to access the effect of the sulfone group on the molecular dimensions and compare this effect with that observed in similar compounds.[1,2]

1. G. A. Jeffrey, Acta Cryst. 4, 58 (1951).
2. R. Desiderato and R. L. Sass, Acta Cryst., in press.

Crystals of the compound suitable for diffraction studies were grown from the melt by sublimation just below the melting point, 236 - 238°C. Weissenberg photographs (CuK_2, λ = 1.5418Å indicated the space group to be either Cc (C_s^4) or C 2/c (C_{2h}^6). The observed systematic absences were $hk\ell$ absent when h + k = 2n + 1 and $h0\ell$ absent when ℓ = 2n + 1. The unit cell dimensions were a = 10.09 (1) A, b = 13.89 (3) A, c= 7.22 (1) A and β = 93.5 (4)°. The density, measured by flotation, was 1.40 g/cc; the theoretical density, calculated on the basis of four molecules per cell, was 1.35 b/cc. Multiple film Weissenberg photographs were taken about the c axis (ℓ = 0-7) and the primitive (a+b)/2 axis ((h+k)/2 = 0-4). Intensities were measured visually. The Lorentz-polarization factor was applied and the data correlated in the usual manner. No corrections were made for extinction or absorption. A total of 605 reflections in the region of reciprocal space considered had detectable intensities.

The trial structure was solved assuming the symmetry to C2/c (C_{2h}^6). Final refinement indicated this assumption to be correct. Because this space group contains eight fold symmetry, the two fold axis of the molecules must coincide with that of the crystallographic unit cell. This information was utilized with a Patterson projection P(u,v) to determine the coordinates of the various atoms. The sulfur atom was quite easily located and the map also contained a moderately well resolved image of the remainder of the

molecule. An electron density projection ρ (x,y) gave a clear image of the molecule nearly in the plane of the projection. The rotation of the molecule out of the projection plane was estimated from the shape of the oxygen peaks and packing considerations. The z parameters of all the atoms were subsequently assigned and structure factors were calculated for all 605 reflections. The reliability index, R, for this trial structure was 0.35. A three dimensional electron density map was synthesized at this point. It was well resolved, showed no spurious peaks and yielded a set of atomic parameters essentially the same as those indicated above. These parameters served as the starting point of the refinement.

The refinement was carried out using the full matrix least squares program ORFLS.[3] The R value was lowered to 0.11 using individual anistropic

3. W. R. Busing, K. O. Martin and H. A. Levy, "ORFLS, A FORTRAN Crystallographic Least Squares Program", ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

temperature factors on each atom. Hydrogen atoms were included in the structure factor calculations with isotropic temperature factors of 5.9. No hydrogen parameters were refined. The weighting scheme used was

$$\sqrt{w} = {}^{1}/F \text{ for } F > 4 \text{ Fmin}$$

$$\sqrt{w} = {}^{1}/4\text{Fmin for } F < 4 \text{ Fmin}$$

The final atomic parameters are listed in Table I. A list of observed and calculated structure factors is available from the authors on request.

The bond lengths and angles calculated from the final atomic parameters are shown in Figure I. This figure is also the view of the molecule projected down the c axis. On the basis of the errors listed in Table I, the largest error in a bond length is 0.02 A and the average error is 0.017 A.

The molecular packing is quite reasonable with no intermolecular distances shorter than the sum of the normally accepted Van der Waals radii.

The sulfur carbon bond distance reported herein as 1.74 A is in good agreement with those found in β isoprene sulfone[1] and cis-2-butene episulfone.[2] The sulfur oxygen bond distance of 1.49 A is in good agreement with the value predicted from the sum of the packing double bond covalent radii but is about 0.05 A longer than that observed in other sulfones. In the remainder of the structure, the bond distances and angles are comparable to the

equivalent values found for fluorene.[4] The ring closing C (6) - C (6')

4. D. M. Burns and J. Iball, Proc. Roy. Soc., Series A., 227, 200 (1955).

distance of 1.46 A is, within experimental error, equal to the value of 1.48 A observed for fluorene. The molecule, within experimental error, possesses C_{2v} symmetry.

Acknowledgments. This work was supported by grants from the National Aeronautics and Space Administration and the Robert A. Welch Foundation of Houston, Texas. The 7094 computer calculations were done at the Common Research Computer Facility located in the Texas Medical Center and supported by USPH Grant FR-00254.

Table I: Final Atomic Parameters (Errors)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B[b]
S[a]	0.0000	.2958(2)	.2500	3.08(16)	2.70(15)	3.05	.00	0.08(8)	0.01	3.12(12)
O	.9771(6)	.2429(4)	.4240(10)	5.84(32)	4.71(30)	4.32	-1.61(14)	-0.71(14)	1.01(16)	5.33(23)
C_1	.1218(8)	.3824(5)	.2897(10)	3.61(32)	3.17(30)	2.05	-0.36(11)	-0.49(17)	-0.24(16)	3.34(23)
C_2	.2566(8)	.3631(7)	.3342(17)	4.38(40)	6.25(46)	4.42	-0.03(19)	-0.43(23)	0.52(24)	5.24(30)
C_3	.3371(10)	.4432(10)	.3691(18)	4.50(44)	8.88(77)	4.98	-1.12(22)	-0.62(24)	0.48(30)	6.09(37)
C_4	.2873(10)	.5363(8)	.3546(16)	9.00(68)	6.87(69)	2.24	-1.98(27)	-0.09(27)	0.36(24)	6.91(39)
C_5	.1545(10)	.5522(7)	.3043(15)	7.18(61)	4.71(46)	3.23	-0.87(19)	0.01(14)	0.12(20)	5.99(36)
C_6	.0716(7)	.4757(5)	.2736(28)	4.30(28)	3.32(30)	2.53	-0.64(14)	0.13(16)	0.14(21)	3.74(23)
H_1[c]	.2874	.3075	.3653							5.88
H_2	.4162	.4362	.3963							5.88
H_3	.3369	.5792	.3681							5.88
H_4	.1189	.6007	.2919							5.88

[a] x and z parameters for sulfur were frozen at value shown

[b] Temperature factors from isotropic refinement, the isotropic temperature factor = $\exp[-1/4(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})]$ or $\exp(-B\sin^2\theta/\lambda^2)$.

[c] All parameters for hydrogen were frozen with C-H = 0.90 A and H-C-C angles equal to 120°.

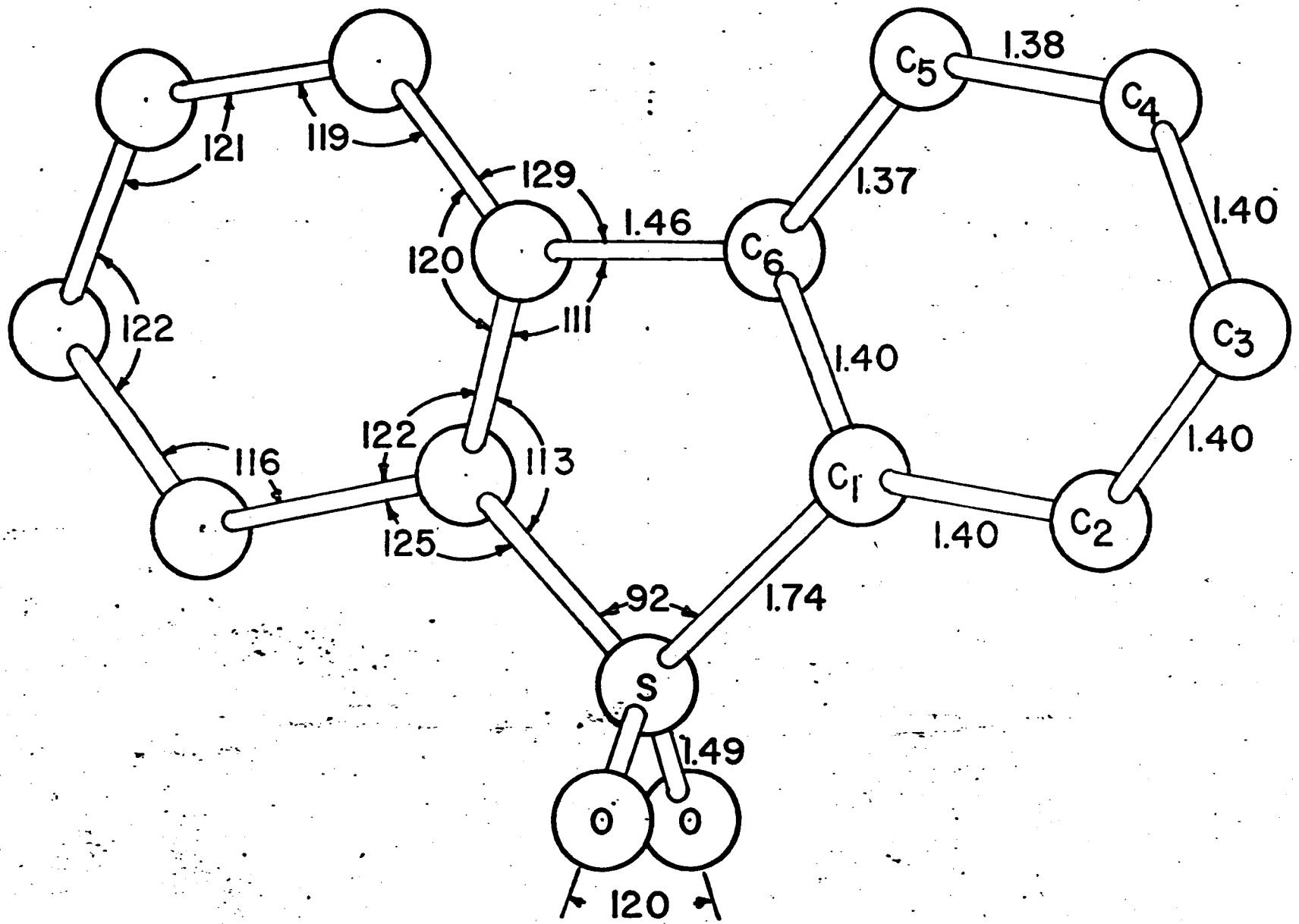

FIGURE I: Bond Distances and Angles